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(54) Title: LOW ENVIRONMENTAL TOXICITY LATEX COATINGS (57) Abstract Combinations of nonvolatile reactive amines, and hydroxyl bearing, unsaturated esters and/or ethers and/or ether-esters (and/or combinations of non-hydroxyl bearing, unsaturated esters and/or ethers and/or ether-esters, and saturated hydroxyl bearing etherified and/or esterified oligomeric glycols and/or oligools), as replacements for conventionally employed volatile amines and/or ammonia as neutralizers, and organic solvents as coalescents respectively, has been found to enable the production of economical, low to no VOC acrylic and vinyl copolymer latex based coatings, paints, and inks. Further enhancement may be had by substitution of hypersurfactants, in place of conventional soaps and/or dispersants and/or detergents, in combination with the aforementioned nonvolatile reactive amines, particularly as particulate dispersants in pigmented and/or reinforced coatings.		

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LOW ENVIRONMENTAL TOXICITY LATEX COATINGS

1 Background of The Invention:

2 The use of ammonia and/or volatile amines as neutralizing
3 agents and/or stabilizers, and of alcohols, glycols, and glycol
4 monoethers and monoesters, often in combination, at levels to 40%
5 by volume (exclusive of water) has been employed for more than
6 fifty years to achieve the coalescence of latex solids in acrylic,
7 polyvinyl acetate and related copolymer resins based coatings.
8 The volatilization of these conventional neutralizers, and
9 coalescing components, after achieving film coalescence is
10 normally required in order to inhibit the resultant film's
11 breakdown (reversion) in the presence of humid environments, and
12 to provide acceptable wear and stain resistance to the dried film.

13 Recent concerns regarding the environmental degradation
14 (predominantly low level ozone formation), and the health and fire
15 hazards associated with exposure to ammonia, volatile amines and
16 volatile organics (VOCs), has led to increasingly strict
17 regulatory limitations on the nature, and proportions, of VOCs
18 which may be employed in coatings. One technique that has been
19 employed in order to comply with said limitations in latex coating
20 applications is the development of self coalescing latex resins
21 which require no coalescents. However, to date, such materials
22 have had the disadvantage of being limited to low Tg film formers
23 with poor performance properties.

24 Subject of The Invention:

25 This invention teaches the use of low levels of combinations
26 of nonvolatile reactive amines, in combination with hydroxyl

1 bearing unsaturated esters and/or ethers and/or ether-esters,
2 and/or non-hydroxyl bearing unsaturated esters and/or ethers
3 and/or ether-esters and incompletely etherified and/or esterified
4 oligomeric glycols and/or oligools as partial or full replacements
5 for conventionally employed volatile amines and/or ammonia as
6 neutralizers, and organic solvents as coalescents, respectively,
7 in latex resin applications. This invention has the advantage of
8 reducing emissions and enhancing the performance of films produced
9 from conventional latex resins, and when employed in conjunction
10 with certain types of hypersurfactants (cf. Table 5) also
11 upgrades pigment and/or extender dispersion, and reduces grind
12 times in particulate containing variants; thus enhancing plant and
13 energy use efficiencies. Synergistic performance enhancement, and
14 VOC reduction in latex resins may be attained via the employment
15 of the aforementioned technologies in combination. Partial
16 replacement of either or of both of the aforementioned components
17 by the alternatives of this invention is shown to provide lesser,
18 but still desirable benefits.

19 Preferred Embodiment of The Invention

20 The non-volatile reactive amines useful in the practice of
21 this invention have vapor pressures below 0.1 mm Hg at 25°C,
22 contain at least one basic nitrogen, and at least one carbon to
23 carbon double bond, and/or a transition metal ligand, and contain
24 no more than twelve carbon atoms per basic nitrogen atom. Those
25 more preferable contain one or more (meth)acryl and/or N-vinyl
26 ligands, and those most preferable have a water solubility

1 exceeding 2% at 25°C. Specific examples of such useful non-
2 volatile reactive amines are given in Table (1). These examples
3 are intended to be illustrative rather than exhaustive of the
4 scope of useful materials.

5
6 TABLE I

- 7 (1A) N-vinyl pyrrolidone
8 (1B) N,N,N'-tris (2-butenyl), ethylene diamine
9 (1C) N', methyl-1, 3-propylene diamine mono 2- propenamide
10 (1D) N, 2-propenyl, bis (2-hydroxy)propyl amine
11 (1E) N, 2-propenyl, N'- (2-hydroxy)ethyl, hexamethylene
12 triamine
13 (1F) 4-(N, 3-hydroxypropyl, N-vinyl) 2-amino ethyl 2-butenate
14 (1G) 2-[N, -(2-oxa-cyclopentadienyl)] amino acetic acid ethyl
15 ester
16 (1H) 4-(N,N bis vinyl) 1,3-pentanediol
17 (1I) tetraethylene glycol mono 3-(N, ethyl) amino, 2-(methyl)
18 2-propenoate
19 (1J) N,N-divinyl glutamic acid 2-propenyl ester
20 (1K) 6-(N,N bis vinyl) hexanoic acid ethyl ester
21 (1L) Titanium IV tetrakis N, 2-aminoethyl ethanolato

22 The preferred types of the hydroxyl bearing, unsaturated
23 esters and/or ethers and/or ether-esters useful in the practice
24 of this invention are those having vapor pressures below 0.1 mm
25 Hg at 25°C, which are capable of air initiated, oxidative
26 oligomerization and/or polymerization derived non-reversible

1 bonding, under normal latex application conditions, to film
2 component(s) and/or to substrate, in order to maximize coating
3 properties via crosslinking the resulting latex thereby
4 minimizing its (post film formation) environmental sensitivity.
5 Examples of such unsaturated esters and ether and ether-esters as
6 are useful in the practice of the instant invention are provided
7 in Table II. These examples are intended to be illustrative
8 rather than exhaustive of the scope of useful materials.

9 Table II

- 10 (2A) trimethylol propane bis (2-methyl)-2-propenoate ester
11 (2B) sorbitan tetrakis 2-butenate ester
12 (2C) bis pentaerythritol 2-propenolate, tris 2-propenoate ester
13 (2D) hexanoic acid 6-hydroxy, (2-propenoate)ethyl ester
14 (2E) citric acid mono isodecenyl ester
15 (2F) malic acid bis cinnamyl ester
16 (2G) 3-heptanoyl furfuryl alcohol
17 (2H) 1,2,3-propanetriol 1-vinyl ether, 2-phenyl carboxylate ester
18 (2J) trimeric 2-butenediol mono (methyl) glutarate ester
19 (2K) ethoxylated (4) bis phenol A mono 2-propenoate ester

20 The preferred types of the non-hydroxyl bearing unsaturated
21 esters and/or ethers and/or ether-esters useful in conjunction with
22 the practice of this invention are those having vapor pressures
23 below 0.1 mm Hg at 25°C, which are capable of air initiated
24 oxidative oligomerization and/or polymerization, and non-reversible
25 bonding, under normal latex application conditions, to film
26 component(s) and/or to substrate, in order to maximize coating

1 properties via crosslinking the resulting latex thereby minimizing
2 its (post film formation) environmental sensitivity. Examples of
3 such non- hydroxyl bearing unsaturated esters and ether and ether-
4 esters as are useful in the practice of the instant invention are
5 provided in Table III. These examples are intended to be
6 illustrative rather than exhaustive of the scope of useful
7 materials.

8 Table III

- 9 (3A) trimethylol propane bis (2-methyl)-2-propenoate ester, mono
10 vinyl ether
11 (3B) 1,2,3-propane triol tris 2-butenate ester
12 (3C) penta erythritol 2-propenolato, tris 2-propenoate ester
13 (3D) hexanoic acid 6-acetoxy, (2-propenoato)ethyl ester
14 (3E) fumaric acid bis isodecyl ester
15 (3F) maleic acid bis cinnamyl ester
16 (3G) furoic acid vinyl ester
17 (3H) 1,2,3-hexanetriol 1,2-bis vinyl ether, phenyl carboxylate
18 ester
19 (3J) trimeric 2-butene-1,4-diol bis propionate ester
20 (3K) ethoxylated (4) bisphenol A bis 2-(methyl)-2-propenoate ester

21 The preferred types of the incompletely etherified and/or
22 esterified oligomeric glycols and/or oligools useful in the
23 practice of this invention are those having vapor pressures below
24 0.1 mm Hg at 25°C, which are oligomers of two to 4 carbon diols,
25 and of three to six carbon triols, wherein each of the ether and/or
26 ester ligands contains five or fewer carbon atoms per oxygen.

1 Examples of such incompletely etherified and/or esterified
2 oligomeric glycols and/or oligoals as are useful in the practice of
3 the instant invention are provided in Table IV. These examples are
4 intended to be illustrative rather than exhaustive of the scope of
5 useful materials.

6 Table IV

- 7 (4A) penta (ethylene glycol) mono methyl ether
8 (4B) tetra (1,4-butylene glycol) mono (2-methyl) butyrate
9 (4C) 1-hydroxy-2,5-bis methyl-3,6,9,12-tetraoxa tetradecane
10 (4D) 4-oxaheptane-1,2,6,7-tetraol mono acetate, mono 2-propyl
11 ether (mixed isomers)
12 (4E) ethoxylated (6) 1,2,4-butanetriol bispropanoate (mixed
13 isomers)
14 (4F) tris 1,2,5-n pentane triol tetraethyl ether (mixed isomers)
15 (4G) tris (1,3-propane-diol) mono isopentyl ether
16 (4H) 1,2- bis (2- hydroxy ethoxy ethyl) 1,2,3-propane triol
17 (4J) polyethylene glycol (300) mono amyl ether
18 (4K) tris neopentyl glycol mono n-propyl ether

19 The surfactants most useful in the practice of this invention
20 are those having vapor pressures below 0.1 mm Hg at 25°C, which are
21 capable of non-reversible bonding, under normal processing
22 conditions, to film component(s) and/or substrate in order to
23 maximize coating properties, while minimizing post film formation
24 environmental sensitivity, and which serve to efficiently wet
25 substrates coated, and to disperse particulates, if any, employed
26 in the formulated latex coating. Among the surfactants found to be

1 useful in the practice of this invention are amphoteric detergents,
2 and certain organometalics based on tetravalent titanium or
3 zirconium. These last have been found to contribute significantly
4 to substrate adhesion and improved corrosion resistance on wood,
5 metallic and ceramic substrates, and to be particularly useful in
6 maximizing color intensities of carbon black, azo and
7 phthalocyanine based pigments. Specific examples of the preferred
8 types of hypersurfactants are given in Table V. These examples are
9 intended to be illustrative rather than exhaustive of the scope of
10 useful materials.

11 Table V

- 12 (5A) 12-N,N,N-trimethylaminododecanoato
13 (5B) N-(pentakis oxyethylene sulfato) triethylene diamine
14 (5C) p-[6-N(methyl) morpholino]octyl phenyl phosphonic acid
15 (5D) N,N,N-triethyl glutamic acid
16 (5E) titanium 4 octyl, [(tris octyl) diphosphato
17 (5F) titanium 4 oxoethylene, bis (dodecyl) phenylsulfonato
18 (5G) oxy [bis titanium 4 (bis tridecyl) diphosphate]
19 (5H) zirconium 4 tetraethylene glycol monomethyl ether, tris
20 (tetraethylene glycol monomethyl ether) diphosphato
21 (5J) zirconium 4, bis w-N,N-(dimethyl)amino octanoato, 1,4-
22 cyclohexanediolato
23 (5K) triethylene glycol diolato, bis [zirconium 4 tris (octyl)
24 phosphate]

25 Those skilled in the art shall no doubt be capable of
26 subverting the teachings of this invention via the substitution of

1 functionally equivalent materials, e.g. employment in combination
2 of hydroxylated and non-hydroxyl bearing esters (ether-esters)
3 optionally in combination with partially esterified and/or
4 etherified glycols, and or polyols, in place of either component
5 (set) alone, (as is amply demonstrated in example No. 4.), or of
6 unsaturated analogous unsaturated amides, for a portion of the
7 aforementioned unsaturated ethers, esters or ether-esters disclosed
8 above, and/or fluorination of one or more of the species of
9 components heretofore described as necessary to the successful
10 practice of this invention; however such non-critical
11 modifications, and/or combinations of relevant species types, must
12 be considered as within the scope of this disclosure.

13 Further amplification of the scope and utility of the instant
14 invention to latex coating applications in inks, paints and stains
15 shall be found to be illustrated by the content(s) of examples 1
16 through 5. Said examples are intended to be illustrative rather
17 than exhaustive of the extraordinarily diverse applicability of the
18 instant invention.

19 Example #1

20 This example teaches the superiority of the present invention
21 versus the prior art with respect to the productivity, VOC
22 emissions, and performance quality in a masonry sealer application.

23 A masonry sealer formulation was prepared by the sequential
24 dispersion of the indicated components (pigment dispersion times
25 and grind quality achievement was noted). The resulting sealer was
26 applied via roller to smooth surface, ten day old, 8" X 18" X 1"

1 thick concrete castings, at an application rate of one gallon per
 2 400 square foot, dry time (to touch) was measured under conditions
 3 of 72° F and 85% humidity. After 240 hours of drying @ 72° F and
 4 85% humidity, sealer performance was measured by weighing the dry
 5 casting, then impounding a 6" depth of water, or alternatively 6%
 6 salt solution, on such a casting for twenty four hours, then
 7 draining and weighing the drained casting. The weight percent of
 8 water, and independently that of 6% salt solution, adsorbed by said
 9 castings were used to determine sealer efficacy. The results of
 10 this study are given in Table No. 1.

11 **Formulation:** in parts by weight; (in order of addition) water
 12 200.0; neutralizer¹, as shown; surfactant^a, as shown, biocides²,
 13 18.50; hydroxy ethyl cellulose, 5.00; potassium tris polyphosphate,
 14 2.00; defoamer², 1.00; coalescent^a, as shown; ultramarine blue
 15 pigment, 0.25; rutile titanium dioxide, 200.0, American process
 16 zinc oxide, 25; platey talc, 250; water, 49.98; AC-625 Acrylic
 17 latex resin³, 352.0; defoamer², 0.98; surfactant^b, coalescent^b, as
 18 shown,; water, 24.99; and sodium nitrite 2.30; thixotrope⁴, as
 19 shown (required) to adjust system viscosity to 85-90 KU at 75° F.

20 Table No. 1

21 <u>Formulation</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
22 neutralizer	amp-95/1.98	1B/2.00	1H/1.80	1G/2.20	1D/1.78
23 surfactant(a)	Tamol 850 ⁷ /14.85	5A/1.80	5E/1.75	5K/1.55	5H/1.50
24 coalescent(a)	Propylene glycol	none	none	4J/4.50	none
25	/34.56				
26 surfactant(b)	Triton N101 ³ /2.20	none	5B/1.00	none	5D/1.25
27 coalescent(b)	Texanol ⁸ /9.88	2A/16.42	3A/12.60	3F/18.55	2H/11.70
28					

1	2	3	4	5	6	7	8	9	10
		<u>Formulation</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>		
3	neutralizer	ammonia/1.00	1B/1.00	1H/1.80	1G/1.20	1D/1.78			
4		1L/1.00	ammonia/1.00	AMP-95/1.00					
5	surfactant (a)	Tamol 850 ⁷ /14.85	5A/1.80	5E/0.75	5K/1.55	5H/0.75			
6	surfactant (b)	Triton N101 ⁶ /2.20	none	Triton N101	none	5D/1.25			
7				/2.20					
8	coalescent (a)	Propylene glycol	none	none	4J/4.50	Propylene glyco			
9		/34.56				/17.88			
10	coalescent (b)	Texanol ⁸ 19.98	2A/16.42	3A/12.60	3F/18.55	2H/5.85			

13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
	<u>Formulation</u>	<u>VOC g/l⁵</u>	<u>Dispersion</u>	<u>Grind</u>	<u>Water</u>	<u>Salt water</u>								
			<u>time hr.</u>	<u>Hegman</u>	<u>adsorption g.</u>	<u>adsorption g.</u>								
16	1	124	3.4	4	46	61								
17	2	8	0.7	6	27	32								
18	3	3	0.6	6	21	28								
19	4	5	0.7	5	24	27								
20	5	4	0.6	6	25	30								
21	6	112	3.1	4	37	48								
22	7	10	0.7	6	32	42								
23	8	3	2.4	5	27	38								
24	9	6	0.7	5	24	27								
25	10	36	1.8	6	31	39								

Notes: a) As shown; 1) A combination of 3.5 parts of Nuosept 95, and 15 parts of Nuocide 404D, Huls Corp. were employed; 2) Defo 806-102; Ultra Inc. 3) AC-625, Union Carbide Corp.; 4) Rhevis CR, Rhevis Corp. 5) via EPA Method 24GC; 6) Rohm and Haas Corp.; 7) Eastman Kodak Inc.

The efficacy of the coalescent systems of the instant art in producing a less water and salt permeable, acrylic latex based masonry seal coating, is compared to a conventionally coalesced counterpart, Formulation No. 1, and is obvious from the preceding data. VOC emissions reduction and improvement in both productivity and dispersion level achieved are likewise self evident.

Example #2

This example teaches the superiority of the present invention versus the prior art with respect to the productivity, VOC

1 emissions, and performance quality in a direct to metal,
2 maintenance coating application.

3 Direct to metal coatings were prepared by the sequential
4 dispersion of the indicated components (pigment dispersion times
5 were noted). The resulting coating was spray applied to sandblasted
6 smooth surface 24" X 8" carbon steel test panels at application
7 rate of one gallon per 250 square feet. After 120 hours of drying
8 @ 72° F and 85% humidity, edge sealing and scribing, the coatings'
9 corrosion resistance performance were each measured by QUV cabinet
10 exposure [cyclic exposure to UV radiation, 4% saline solution, and
11 varying temperature (25°-80° C)].

12 **Formulation:** in parts by weight (in order of addition): water,
13 50.0; neutralizer, as shown; Surfactant^a, as shown, biocide¹, 4.00;
14 oxidized polyethylene wax, 4.00; (disperse wax) polyurethane
15 thixotrope², as shown; defoamer³, 2.00; coalescent^a, as shown,
16 ultramarine blue pigment, 0.25; rutile titanium dioxide, 125; zinc
17 aluminate 150; Acrylic latex resin⁴, 64.0; (disperse particulates
18 to Hegman 7.5+). Neutralizer, is shown; acrylic latex resin⁴,
19 564.0; defoamer², 0.98; surfactant^b, coalescent^b, as shown; water,
20 16.00; arid sodium nitrate 2.30. Thixotrope², (as required) to
21 adjust system viscosity to 80-85 KU at 75° F . The control coating
22 required 3.7 hours to disperse to a Hegman grind gauge reading of
23 7+, whereas each of the instant art coatings achieved said fineness
24 of grind in less than one half hour. The results of this study are
25 given in Table No. 2

Table No. 2

<u>Formulation</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
neutralizer	DMAMP-80 ⁵ /12.5	1A/4.00	1C/1.80	1E/2.20	1J/1.78	DMAMP-80 ⁵ /6.25
surfactant (a)	Triton CF10 ⁶ /10.00	5D/1.80	5F/1.75	5C/1.55	5J/1.50	1A/ 2.00
thixotrope ²	15.00	5.00	5.50	8.70	5.30	Triton CF 10/5.00
coalescent (a)	Diproylene glycol /34.60	4B/12.00	4E/10.5	4K/8.25	none	9.32
surfactant (b)	none	none	5A/1.00	Triton CF10 ⁶ .4.0	none	5D/1.25
coalescent (b)	PmPE ⁷ /44.60	2A/16.42	3A/12.60	3F/18.55	2H/14.70	2H/14.70
thixotrope ²	21.40	3.20	1.50	0.70	2.30	1.95
<u>Formulation</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
neutralizer	DMAMP-80 ⁵ /12.5	1A/4.00	1C/1.80	1E/2.20	1J/1.78	DMAMP-80 ⁵ /6.25
surfactant (a)	Triton CF10 ⁶ /10.00	5D/1.80	5F/1.75	5C/0.55	5J/1.50	Triton CF10/5.00
surfactant (b)	none	none	5A/1.00	Triton CF10 ⁶ /2.0	none	5D/1.25
thixotrope ²	15.00	5.00	5.50	8.70	5.30	9.32
coalescent (a)	Dipropylene glycol /17.3	PmPE ⁷ /22.60	4B/12.00	4E/10.5	4K/8.25	PmPE ⁷ /22.3
coalescent (b)	2A/ 8.81	2A/ 6.42	PmPE ⁷	3F/ 18.55	2H/14.70	2H/14.70
thixotrope ²	18.90	6.20	4.50	3.70	2.30	6.95

<u>Formulation</u>	<u>VOC g/l⁸</u>	<u>Initial gloss</u>	<u>60° gloss @</u>	<u>60° gloss @</u>	<u>60° gloss @</u>
		<u>@60°</u>	<u>200hr. QUV</u>	<u>500 hr. QUV.</u>	<u>1,000 hr. QUV</u>
1	232	82	76	31	film destroyed
2	9	91	87	82	76
3	11	93	90	88	80
4	8	87	86	82	61
5	10	88	86	85	84
6	13	84	80	66	59
7	72	85	79	46	12
8	57	80	76	51	18
9	28	87	84	72	63
10	7	88	86	84	78
11	8	92	90	87	85
12	77	85	80	75	48

Notes: 1) Nuosept 95, -Huls Corp. 2) Acrysol RM 2020, Rohm and Haas 3) Defo 3000; Ultra Inc. 4) HG 56, Rohm and Haas Corp. 5) 80%

1 2-N,N-dimethylamino-2-methyl propanol aq. 6) Union Carbide Corp. 7)
2 propylene glycol mono phenyl ether. 8) via EPA Method 24GC

3 The efficacy of the coalescent systems of the instant art in
4 producing a more environmentally resistant, acrylic latex based
5 direct to metal coating, as compared to a conventionally coalesced
6 counterpart, Formulation No. 1, is obvious from the preceding data.
7 VOC emissions reduction, and improvement in productivity achieved
8 are likewise self evident.

9 Example #3

10 This example teaches the superiority of the present invention
11 versus the prior art with respect to productivity, VOC emissions,
12 and performance quality in a polyvinyl acetate based interior flat
13 architectural paint application.

14 Interior flat paints, were prepared by the sequential
15 dispersion of the indicated components (pigment dispersion times,
16 and dispersion efficacy were noted). The resulting coating was
17 brush applied to unprimed drywall (gypsum sheet) @ 72° F and 80%
18 humidity, coverage, stain removal, and scrubability performance
19 were each measured after 7 days of drying 72+/- 2° F @ 65-80%
20 humidity.

21 Formulation; in parts by weight; (in order of addition) water,
22 200.0; neutralizer¹, as shown; surfactant^a, as shown, biocides²,
23 1.00; hydroxy ethyl cellulose, as shown; potassium tris
24 polyphosphate, as shown; defoamer³, 1.00; coalescent^a, as shown;
25 ultramarine blue pigment, 0.25; rutile titanium dioxide, 250.0,
26 water washed clay⁴, 50.0; calcium carbonate⁵, as shown; diatomite⁶,

1 50.0; water, 49.98; PVA latex resin⁷, 352.0; defoamer², 0.98;
 2 coalescent^b, as shown ; water, 100 .0;and sodium nitrite 2.30;
 3 thixotrope⁸, as shown (required) to adjust system viscosity to 90-
 4 100 KU at 75° F.

5 The results of this evaluation are shown in Table No. 3.

6 Table No. 3

7	Formulation	1	2	3	4	5	6
8	neutralizer	28% ammonia aq.	1B/2.00	1H/1.80	1G/2.20	1D/1.78	28% ammonia
9		6.05					6.05
10	HEC(QP-4400)	5.50	1.20	1.35	1.25	1.40	1.35
11	surfactant(a)	Tamol 731/6.90	5E/1.80	5J/1.75	5C/1.55	5F/1.5	Tamol 731/6
12		Triton N101/3.31					Triton
13							N101/3.31
14	coalescent(a)	Propylene glycol	4A/6.00	4 F/7.00	4H/5.50	4E/7.00	4E/7.00
15		/51.95					
16		Texanol/9.88					
17	Calcite	50	150	125	150	140	50
18	coalescent(b)	none	2A/26.4	3C/12.60	3F/18.50	2J/11.90	2J/11.90
19	thixotrope ^a	3.5	3.0	3.1	2.7	2.4	3.9
20							
21	Formulation	7	8	9	10		
22	neutralizer	28% ammonia aq.	1B/2.00	1H/1.80	1H/1.80		
23		6.05					
24	HEC (QP-4400)	5.50	1.20	1.35	1.25		
25	surfactant(s)	Tamol 731/ 6.9	Tamol 731/ 3.9	5J/ 1.75	Tamol 731/ 6.9		
26		Triton N101/ 3.31	5J/1.0		Triton N101/ 3.		
27	coalescent (a)	Propylene glycol	4A/6.00	Propylene glycol	4H/5.50		
28		51.95		51.95			
29	calcite	50	100	125	150		
30	coalescent (b)	4E/2.00	2A/ 26.4	3C/ 12.60	3F/ 18.50		
31	thixotrope ^a	3.5	3.0	3.1	2.7		
32							
33							
34	Formulation	VOC g/l ⁹	Dispersion Time	Grind	Min.Coalescence	Scrubs ¹⁰	Stain Removal ¹¹
35		hr.		Hegman	temp °C		
36							
37	1	199	2.4	4	47	410	6
38	2	8	0.4	5	34	1,740	9
39	3	3	0.6	6	32	2,025	10
40	4	5	0.6	6	36	1,960	9
41	5	4	0.5	5	30	2,230	10
42	6	15	2.2	4	31	785	8
43	7	190	2.4	4	43	850	7
44	8	9	0.9	5	35	1,140	8
45	9	188	1.1	5	45	890	7
46	10	8	2.4	4	37	1,310	8
47							

48 Notes: 1) As shown; 2) Nuosept 95, Huls Corp.; 3) Defo 3000; Ultra
 49 Inc.. 4) 70C Huber Corp.5) Camel Carb., Cambel Corp.; 6) Diafil 530

viscosity of 65-70 KU, and the coating was applied by curtain coating on sanded but unprimed 4' X 8' X 0.25" laminate natural oak (on pine) substrate. The coated panels were force dried by passing same through a 180° F oven for 20 minutes, then cooled at ambient temperature (ca. 80° F) for 24 hours prior to evaluation, for abrasion and solvent resistance. to determine coating performance, efficacy. The results of this study are given in Table No. 4.

Table No. 4

Formulation	1	2	3	4	5	6	7	8
Part A:								
neutralizer	28%	1A	1H	1H	1H	1B	1B	1B
	ammonia aq.							
Part B: formulation								
Texanol	8.00						4.00	4.00
diethylene glycol	18.20						9.10	9.10
mono butyl ether								
2A		12.05	6.00		6.00	6.00	6.00	
2C			4.40	10.70				
3B					4.20			6.00
4G			1.90	2.90	1.05	6.20		
4J								
Formulation	VOC g/l ¹ resistance ²	Abrasion resistance ³	Solvent resistance ⁴	Stain hr. @ 80°F ⁵	Mix pot life			
1	165	114	lifts	poor	7.5			
2	3	31	slight softening	good	42			
3	4	29	slight softening	fair	35			
4	3	24	no change	excellent	40			
5	3	26	no change	good	61			
6	4	98	mod. Softening	fair	46			
7	83	19	slight softening	fair	21			
8	85	78	severe softening	poor	11			

Notes: 1) By EPA Method 24GC; (formulations 2 through 7 produced 0 to negative VOC readings by EPA Methods 24, and 24A; 2) Tabor CS-10 wheel 1000 cycles; 3) 24 hr methyl ethyl ketone covered spot test; 4) 24 hr exposure to lipstick; 5) time to 10% loss of abrasion resistance in finished coating.

This example demonstrates, that the use of the combination of components cited as the basis of the instant invention, viz. That

1 Whittaker, Clark, and Daniels Inc. 7) Rhoplex 3077, Rohm and Haas
2 Corp.; 8) Rhevis CR, Rhevis Corp. 9) via EPA Method 24GC. 10) ASTM
3 method; 11) ASTM method.

4 The efficacy of the coalescent systems of the instant art in
5 producing a more, scrub and stain resistant PVA latex based
6 interior flat architectural coating as compared to a conventionally
7 coalesced counterpart, Formulation No. 1, is obvious from the
8 preceding data. VOC emissions reduction and improvement in both
9 productivity and dispersion level achieved are likewise self
10 evident, as is a considerable reduction in minimum coalescence
11 temperature, without recourse to the use of low boiling, flammable
12 solvent(s), normally employed to induce same.

13 Example #4

14 This example teaches the superiority of the present invention
15 versus the prior art with respect to the productivity, VOC
16 emissions, and performance quality in a force dried, clear,
17 protective, two component acrylic latex cured - waterborne epoxy,
18 wood cabinet coating.

19 Component A. neutralizing agent, as shown-3.5 PBW; sodium
20 nitrite 0.15 and defoamer (Patcote 519-Patco Coatings Inc.) were
21 admixed with 95.85 PBW of (Acrylic latex-Maincote AE 58), and said
22 emulsion was subsequently mixed with 50 PBW of Component B,
23 formulated by blending various additives, as shown, into 12.5 PBW
24 of Genepoxy 370-H55- Daubert Chemical Co., and diluting as
25 necessary with water to produce a total part B weight of 25 parts.
26 Thixatrop¹, was added, as required, to provide an initial mix

1 nonvolatile reactive amines, in combination with hydroxyl bearing
2 unsaturated esters and/or ethers and/or ether-esters, and/or non-
3 hydroxyl bearing unsaturated esters and/or ethers and/or ether-
4 esters and incompletely etherified and/or esterified oligomeric
5 glycols and/or oligools as (partial or full) replacements for
6 conventionally employed volatile amines and/or ammonia as
7 neutralizers, and organic solvents as coalescents, respectively may
8 be employed to substantially enhance the processability (pot life),
9 mechanical and chemical resistance properties (abrasion and stain
10 resistance respectfully) as well as attain VOC reduction in wood
11 coatings. A further benefit of the instant invention as applied to
12 wood coatings is that unlike conventionally coalesced waterborne
13 coatings, e.g. formulation D-1 latex formulations based upon the
14 teachings of this invention, e.g. formulations D-2 through D-7, do
15 not cause significant grain rise, thereby virtually eliminating the
16 necessity for intercoat sanding. These data also demonstrate that
17 subsets of the preferred combination of components herein disclosed
18 (e.g. formulations D-3, D-5, and D-6) may provide considerable
19 benefits relative to their conventional counterparts, such as
20 Formulation No. 1; however, omission of one or more of the
21 components of the combination herein disclosed leads to inferior
22 results as compared to the inclusion of the full compliment.

23 Example #5

24 This example teaches the superiority of the present invention
25 versus the prior art with respect to the productivity, VOC
26 emissions, and performance quality in waterborne flexographic inks.

1 A latex flexographic ink formulation, was prepared by the
 2 sequential dispersion of the indicated components (pigment
 3 dispersion times and grind quality achievement was noted). The
 4 resulting ink was applied via a #6 wire wound rod to bond paper,
 5 and permitted to dry. Dry time (to touch) was measured under
 6 conditions, of 72° F and 85% humidity. After 6 hours of drying @,
 7 72° F and 85% humidity, heat seal resistance performance (face to
 8 face) was measured at 25 psig. and 2 seconds contact time) the
 9 results of this study are given in Table No. 5.

10 **Formulation:** in parts by weight; (in order of addition) E-2350
 11 resin 267; neutralizer, as shown; surfactant, as shown; Defo 1020
 12 defoamer 4.00 Ultra Inc.; coalescent^a, as shown; calcium lithol
 13 pigment 50% presscake, 400-Sun Chemical Corp.; Michemlube wax 5-
 14 Michelman Inc., water, as required in order to produce a viscosity
 15 of 27 seconds using a #2 Zahn cup. Relative dry ink color
 16 intensities were measured by integrating thin film reflectance
 17 spectra at 300-600 um wavelengths using a spectrophotometer after
 18 48 hours of drying at the above conditions

Table No. 5

<u>Formulation</u>	<u>1</u>	<u>2</u>	<u>3</u>
neutralizer	28% ammonia aq, 2.00	1D/2.00	1H/1.40
surfactant	Tamol 850/4.95	5A/1.80	5E/1.75
coalescent	isopropanol/48 Texanol/24	2A/10.5 3C/15.5 4H/5.5	2E/20.0
<u>Formulation</u>	<u>4</u>	<u>5</u>	<u>6</u>
neutralizer	1F/2.00	1D/1.46	28% ammonia aq/2.00
surfactant	5K/1.55	5H/1.50	Tamol 850/ 4.95
coalescent	3C/25.0	3C/18.0 4H/7.0	3C/18.0 4H/7.0

	<u>Formulation</u>	<u>VOC g/l⁵</u>	<u>Dry to touch time</u> <u>hr.</u>	<u>6 hr. Heat seal</u> <u>resistance °C</u>	<u>Relative color</u> <u>intensity.</u>
1					
2					
3					
4					
5	1	144	3.4	86	1.00
6	2	4	0.7	154	1.42
7	3	3	0.6	172	1.27
8	4	5	0.7	104	1.08
9	5	4	0.6	167	1.39
10	6	7	0.6	122	1.03

11

12 Notes: The efficacy of the coalescent systems of the instant

13 art in producing a faster drying, more strongly colored, and

14 lower VOC acrylic latex based printing ink coating as compared to

15 a conventionally coalesced counterpart are obvious from the

16 preceding data, as are indications that incomplete application of

17 the teachings of this disclosure may lead to inferior results.

18 Note the deficiencies in the heat seal performance of formulation

19 E-4 as compared to E-2, E-3, and E-5, the benefits of

20 hyperdispersant use as indicated E-2 to E-5 vs. E-6.

21 Example #6

22 This example teaches the utility of the instant

23 invention in the production of superior waterborne anti-scuff

24 overprint coatings for graphic arts applications.

25 A 30% solution of water reducible styrene-acrylic copolymer resin

26 in water was prepared by admixture of the indicated neutralizing

27 agent-as shown, water, and Air Product Corp's Flexbond 28 resin.

28 Thirty parts by weight (PBW) of the preceding solution, were

29 admixed with 50 PBW of styrene- acrylic latex resin (Flexbond

30 285, Air Products Corp.), coalescent, and surfactant(s) -as

31 shown, poly ethylene wax, 2 PBW, and sufficient water to dilute

32 the system to 100 PBW.

1 The resulting coating was applied, in line on a high speed six
2 color lithographic cold web press, to a solid four color print
3 pattern, followed by in line infrared drying, and folding.

4 Measurements of VOC (by EPA Method 24), offset, and blocking
5 limited maximum allowable impression rates (impressions/ minute
6 [IPM]), were made. The results are given in Table 6.

7 Table 6

8	<u>Formulation</u>	<u>1</u>	<u>2</u>	<u>3</u>
9	neutralizer	28% ammonia/ 6.00	AMP 95 ¹ / 8.00	AMP 95/ 8.00
10	coalescent (s)	isopropanol/ 12	isopropanol/ 12	2G/ 4.50
11	surfactant	Tamol 850/ 2.05	Tamol 850/ 2.05	5K/ 0.75
12				
13	<u>Formulation</u>	<u>4</u>	<u>5</u>	<u>6</u>
14	neutralizer	1G/ 6.00	1G/ 6.00	1G/ 6.00
15	coalescent (s)	2G/ 4.50	2G/ 4.50	3C/ 3.65
16				4C/ 0.85
17	surfactant	Tamol 850/ 2.05	5K/ 0.75	2K/ 0.75
18				
19	<u>Performance</u>	<u>1</u>	<u>2</u>	<u>3</u>
20				
21	VOC -g/l.	131	146	27
22	max IPM (offset)	8,240	9,235	12,720
23	max IPM (block)	10,150	9,950	14,610
24				
25	<u>Performance</u>	<u>4</u>	<u>5</u>	<u>6</u>
26				
27	VOC -g/l.	3	4	4
28	max IPM (offset)	16,670	18,000 ²	18,000
29	max IPM (block)	17,130	18,000	18,000
30				
31				

1 Claims:

2 What we claim is:

3 1) Compositions of matter comprising:

4 essentially nonvolatile reactive amines;

5 hydroxyl bearing, unsaturated esters and/or ethers and/or

6 ether-esters; and/or

7 combinations of non-hydroxyl bearing, unsaturated esters

8 and/or ethers and/or ether-esters, and/or saturated hydroxyl

9 bearing etherified and/or esterified oligomeric glycols

10 and/or oligools.

11 2) Compositions of matter comprising:

12 volatile amines and/or ammonia neutralizers;

13 hydroxyl bearing, unsaturated esters and/or ethers and/or

14 ether-esters; and/or

15 combinations of non-hydroxyl bearing, unsaturated esters

16 and/or ethers and/or ether-esters, and/or saturated hydroxyl

17 bearing etherified and/or esterified oligomeric glycols

18 and/or oligools.

19 3) Compositions of matter comprising:

20 essentially nonvolatile reactive amines; and

21 organic solvent coalescents.

22 4) Compositions of matter as defined in Claims 1, 2 and 3 having
23 as an additional component latex resin.

24 5) Compositions of matter as defined in Claims 1, 2, 3 and 4
25 having hypersurfactants as an additional component.

26 6) Compositions of matter as defined in Claim 5 in which the

1 hypersurfactants are derived from titanium or zirconium based
2 organometalics.

3 7) Compositions of matter as in Claim 4 in which the latex resin
4 is derived from poly vinyl acetate and/or acrylic and/or a
5 copolymer thereof.

6

7

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(72) Inventor: SUGERMAN, Gerald [US/US]; 8 Cambridge Drive, Allendale, NJ 07401 (US).
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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: LOW ENVIRONMENTAL TOXICITY LATEX COATINGS


(57) Abstract: Combinations of nonvolatile reactive amines, and hydroxyl bearing, unsaturated esters and/or ethers and/or ether-esters (and/or combinations of non-hydroxyl bearing, unsaturated esters and/or ethers and/or ether-esters, and saturated hydroxyl bearing etherified and/or esterified oligomeric glycols and/or oligools), as replacements for conventionally employed volatile amines and/or ammonia as neutralizers, and organic solvents as coalescents respectively, has been found to enable the production of economical, low to no VOC acrylic and vinyl copolymer latex based coatings, paints, and inks. Further enhancement may be had by substitution of hypersurfactants, in place of conventional soaps and/or dispersants and/or detergents, in combination with the aforementioned nonvolatile reactive amines, particularly as particulate dispersants in pigmented and/or reinforced coatings.

WO 1999/032563 A3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/24224

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : A01N 43/16 US CL : 514/451 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 514/451 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,343,884 A (MULLER et al.) 10 August 1982 (10.08.1982), see entire document.	1-7
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:		
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"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	
"O" document referring to an oral disclosure, use, exhibition or other means	"Z" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 04 April 2005 (04.04.2005)	Date of mailing of the international search report 08 APR 2005	
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230	Authorized officer Harry C Kim  Telephone No. 703-305-3257	

ACCESSION NUMBER: 1982:34816 CAPLUS
 DOCUMENT NUMBER: 96:34816
 TITLE: Stabilization of alkenylanilines
 PATENT ASSIGNEE(S): Mitsui Toatsu Chemicals, Inc., Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 5 pp.
 CODEN: JKXXAF
 DOCUMENT TYPE: Patent
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JP 56115745	A2	19810911	JP 1980-18572	19800219
JP 62003834	B4	19870127		

PRIORITY APPLN. INFO.: JP 1980-18572 19800219

AB Alkenylanilines in mixture with phenols were stabilized by addition of >10 weight%

saturated aliphatic alcs., ethers, esters, or aromatic alcs. Thus, 100 weight parts of

an 1:1 mixture of PhOH and 4-isopropenylaniline (99.5% purity) was mixed with 100 weight parts HOCH₂CH₂OH and the mixture kept 6 h at 50° to show 1.0% polymer and 0.1% 2-(4-hydroxyphenyl)-2-(4-aminophenyl)propane, vs. 55.2 and 40.1%, resp., without a stabilizer.

IT 54518-03-5

RL: RCT (Reactant); RACT (Reactant or reagent)
(stabilizer, for alkenylaniline)

RN 54518-03-5 CAPLUS

CN 1-Propanol, 3-[3-(1-methylethoxy)propoxy]- (9CI) (CA INDEX NAME)

i-PrO-(CH₂)₃-O-(CH₂)₃-OH

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